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|--|--|--|---------------------|--|---------------------|
| FORM PTO1390<br>OFFICE<br>(REV 10-92)  |  | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK                         |                     | Express Mail Label Number:<br><b>ET825363436US</b><br>ATTORNEY'S DOCKET NO<br><b>1999DE507</b><br><b>10/070071</b> |                     |
| TRANSMITTAL LETTER TO THE UNITED STATES<br>DESIGNATED/ELECTED OFFICE (DO/EO/US)  |  |  |                     |  |                     |
| INTERNATIONAL APPLICATION NO.<br><b>PCT/EP00/08538</b>   | INTERNATIONAL FILING DATE<br><b>01/09/2000</b><br><b>(01 September 2000)</b>   | PRIORITY DATE CLAIMED<br><b>03/09/1999</b><br><b>(03 September 1999)</b> |                     |  |                     |
| TITLE OF INVENTION<br><b>Low Viscous Cellulose Ethers That Flocculate in Hot Water, Method for the Production Thereof and Their Use</b>  |  |  |                     |  |                     |
| APPLICANT(S) FOR DO/EO/US: <b>Alf HAMMES</b>   |  |  |                     |  |                     |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items under 35 U.S.C. 371.  |  |  |                     |  |                     |
| 1 <input checked="" type="checkbox"/> This express request to immediately begin national examination procedures (35 U.S.C. 371(f)).  |  |  |                     |  |                     |
| 2 <input checked="" type="checkbox"/> The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees as follows:   |  |  |                     |  |                     |
| CLAIMS   | (1)<br>FOR   | (2)<br>NUMBER FILED  | (3)<br>NUMBER EXTRA | (4)<br>RATE  | (5)<br>CALCULATIONS |
|  | TOTAL CLAIMS   | 17 - 20 =  | 0                   | X \$18.00  |                     |
|  | INDEPENDENT CLAIMS   | 3- 3 =   | 0                   | X \$84.00  |                     |
|  | MULTIPLE DEPENDENT CLAIMS (if applicable)  |  |                     | +  | 280.00              |
|  | BASIC NATIONAL FEE (37 CFR 1.492(a) (1)-(4):<br><input checked="" type="checkbox"/> For filing with EPO or JP search report (37 CFR 1.492(a)(5))   |  |                     | \$   | 890.00              |
|  | International Preliminary Examination fee paid to USPTO (37 CFR 1.482)   |  |                     |  | 740.00              |
|  | No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))  |  |                     |  | 710.00              |
|  | Neither international preliminary examination fee paid to USPTO (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO   |  |                     |  | 1,040.00            |
|  | International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Articles 33(2)-33(4)   |  |                     |  | 100.00              |
|  | Surcharge of \$135.00 for furnishing the National fee or oath or declaration later than <u>20</u> <u>30</u> months from the earliest claimed priority date (37 CFR 1.492(e)).                          |  |                     |  |                     |
|  | TOTAL OF ABOVE CALCULATIONS  |  |                     |  | = \$ 1170.00        |
|  | SUBTOTAL   |  |                     |  | + \$ 1170.00        |
|  | Processing fee of \$135.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). |  |                     |  |                     |
|  | TOTAL NATIONAL FEE   |  |                     |  | \$1170.00           |
|  | Fee for recording the enclosed assignment (37 CFR 1.21(h)).  |  |                     |  | + 0.00              |
|  | TOTAL FEES ENCLOSED  |  |                     |  | \$1170.00           |
| a. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>03-2060</u> in the amount of \$ <u>1170.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed.                                       |  |  |                     |  |                     |
| b. <input checked="" type="checkbox"/> The Commissioner is authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>03-2060</u> . A duplicate copy of this sheet is enclosed. |  |  |                     |  |                     |

|  |                                     |  |   |
|--|-------------------------------------|--|---|
| 3  | <input checked="" type="checkbox"/> | A copy of the International Application as filed (35 USC 371(c)(2))  |   |
|  |                                     | a.   | is transmitted herewith (required only if not transmitted by the International Bureau) and English translation  |
|  |                                     | b.   | is not required, as the application was filed in the US Receiving Office (RO/US)  |
|  |                                     | c.   | <input checked="" type="checkbox"/> has been transmitted by the International Bureau.   |
| 4.   | <input checked="" type="checkbox"/> | A translation of the International Application into English (35 USC 371(c)(2)).  |   |
| 5  |                                     | Amendments to the claims of the International Application under PCT Article 19 (35 USC 371(c)(3)).   |   |
|  |                                     | a.   | Are transmitted herewith (required only if not transmitted the International Bureau)  |
|  |                                     | b.   | Have been transmitted by the International Bureau   |
| 6.   |                                     | A translation of the amendments to the claims under PCT Article 19 (35 USC 371(c)(3)).   |   |
| 7.   |                                     | An oath or declaration of the inventor (35 USC 371(c)(4)).   |   |
| 8.   | <input checked="" type="checkbox"/> | A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 USC 371(c)(5)).  |   |
| Other document(s) or information included:   |                                     |  |   |
| 9.   |                                     | An information Disclosure Statement under 37 CFR 1.97 and 1.98.  |   |
| 10   |                                     | An assignment document for recording. Please mail the recorded assignment document to the person whose signature, name and address appears at the bottom of this page. |   |
| 10.1   |                                     | A copy of the International Filing Receipt.  |   |
| 10.2   |                                     | A copy of the International Search Report.   |   |
| 10.3   | <input checked="" type="checkbox"/> | A copy of the International Preliminary Examination Report.  |   |
| 10.4   |                                     | A copy of Form PCT/IB/306 - Notification of the Recording of a Change  |   |
| 10.5   |                                     | Preliminary Amendment deleting multiple dependent claims.  |   |
| 11.  | <input checked="" type="checkbox"/> | The above checked items are being transmitted:   |   |
|  |                                     | <input checked="" type="checkbox"/>  | by thirty (30) months and a proper demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. |
| 12   |                                     | At the time of transmittal, the time limit for amending claims under Article 19:   |   |
|  |                                     | a.   | <input checked="" type="checkbox"/> has expired and no amendments were made.  |
|  |                                     | b.   | has not yet expired.  |
| 13.  |                                     | Certain requirements under 35 USC 371 were previously submitted by the applicant on _____, namely:   |   |
| <p><u>Anthony A. Bisulca</u> Date: <u>March 1, 2002</u></p> <p>Anthony A. Bisulca, Registration No. 40,913<br/> Clariant Corporation<br/> 4331 Chesapeake Drive<br/> Charlotte, North Carolina 28216<br/> Telephone: 704/395-6701<br/> Facsimile: 704/395-6727</p> |                                     |  |   |

Attorney's Docket No. 15 E507

533P DPCT/PTO 27 JUN 2002 #5

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re new U.S. patent application of  
Aif HAMMES  
Serial No. 10/070,071  
Filed: March 1, 2002  
For: LOW-VISCOUS CELLULOSE ETHERS THAT FLOCCULATE IN HOT WATER;  
METHOD FOR THE PRODUCTION THEREOF AND THEIR USE

Attn: Box Missing Parts

RESPONSE TO NOTICE TO FILE MISSING PARTS OF APPLICATION

Assistant Commissioner for Patents  
Washington, D.C. 20231

Dear Sir,

In response to the Notice to File Missing Parts of Non-Provisional Application dated May 1, 2002, submitted herewith for filing in the above-identified application is the executed Declaration. A copy of the PTO form is also enclosed.

The Commissioner is hereby authorized to charge the surcharge due (37 CFR 1.16(e)) in the amount of \$130.00 to Deposit Account No. 03-2060. The Commissioner is also authorized to charge any fee deficiency asserted to be paid, or which should have been paid herewith, or with any paper hereafter filed in this application and credit any fee overpayment to Deposit Account No. 03-2060.

Respectfully submitted,

  
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CERTIFICATE OF MAILING/TRANSMISSION (37 CFR 1.8a) and 1.10

I hereby certify that this correspondence is, on the date shown below, being transmitted by facsimile to the Assistant Commissioner for Patents, (Fax No. (703) 308-7751 (Initial Patent Examination Division) (5 pages)

10070071  
Vicki E. Sgro  
Date: June 27, 2002

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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Express Mail Label Number: **ET825363436US**

ET 825363436 US

Date of Mailing: March 1, 2002

**CERTIFICATION UNDER 37 CFR 1.10**

I hereby certify that on the date indicated above this International application and the documents referred to as enclosed therein, of:

**Inventor: Alf HAMMES**

**For: LOW-VISCOUS CELLULOSE ETHERS THAT FLOCCULATE IN HOT WATER, METHOD FOR THE PRODUCTION THEREOF AND THEIR USE**

**International Application No.: PCT/EP00/08538**

**International Filing Date: 01 September 2000**

**Priority Filing Date: 03 September 1999**

is being deposited with the United States Postal Service as "Post Office to Addressee"

Express Mail addressed to the Assistant Commissioner for Patents, Attention: Box PCT (DO/EO/US), Washington, D.C. 20231 in accordance with 37 CFR 1.10.

Vicki L. Sgro



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. :

U.S. National Serial No. :

Filed :

PCT International Application No. : PCT/EP00/08538

VERIFICATION OF A TRANSLATION

I, Susan POTTS BA ACIS

Director to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare:

That the translator responsible for the attached translation is knowledgeable in the German language in which the below identified international application was filed, and that, to the best of RWS Group plc knowledge and belief, the English translation of the international application No. PCT/EP00/08538 is a true and complete translation of the above identified international application as filed.

I hereby declare that all the statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application issued thereon.

Date: 28 February 2002

Signature of Director :

For and on behalf of RWS Group plc

Post Office Address :

Europa House, Marsham Way,  
Gerrards Cross, Buckinghamshire,  
England.

WO01/18062

1

**10/070071**  
JC19 Rec'd PCT/PTO 01 MAR 2002

Low-viscosity, hot water-coagulable cellulose ethers, process for the preparation thereof by depolymerization, and the use thereof

- 5 The present invention relates to low-viscosity, hot water-coagulable cellulose ethers of high purity and high whiteness, to a process for the preparation of these cellulose ethers by depolymerization by means of acid-catalyzed, hydrolytic degradation, where appropriate in the presence of an oxidizing agent, and to the use thereof.

10

The degradation of cellulose ethers with high degrees of polymerization has been known for a long time and can be achieved in diverse ways. In particular, degradation to very low-viscosity products has attracted great attention since these products can be employed advantageously inter alia as coating material for

15 active pharmaceutical ingredients or seeds, but also, for example, in suspension polymerization. Cellulose ethers whose Höppler viscosity, measured as 2.0% solution (absolutely dry) in water at 20°C, is not more than 50 mPas are referred to hereinafter as very low-viscosity products.

- 20 The processes employed for degrading cellulose ethers include, besides acid-catalyzed hydrolytic cleavage of the acetal linkage, inter alia oxidative degradation and degradation by high-energy radiation or microorganisms/enzymes.

- The reduction in the viscosity of cellulose ethers by irradiation with high-energy
- 25 radiation is described, for example, in DE-A-44 34 280 and US-A-2 895 891. Salt-free cellulose ethers are also crosslinked instead of degraded if suitable reaction conditions are chosen. The disadvantages of the process are essentially the production of inhomogeneous materials (dependence of the degree of polymerization on the layer thickness irradiated, depth of penetration of the
- 30 radiation, radiation intensity), the impossibility of removing by-products of the reaction from the mixture, and the radiation treatment which is generally exposed to public criticism.

Processes for the oxidative degradation of cellulose ethers are described inter alia in US-A-2 912 431, US-A-4 316 982, CH-B-461 455, DE-A-20 16 203 and GB-B-953 944.

- 5 US-A-2 912 431 describes a process in which hypohalites, peroxides or periodates degrade carboxymethylcelluloses in a mixture with aqueous alcohol at 40 to 80°C with simultaneous bleaching.

The degradation of cellulose ethers which are moist with water and have a dry content of 40 to 75% using ozone/air/oxygen mixtures at 0 to 60°C is described in

- 10 US-A-4 316 982. CH-B-461 455 describes a process in which the cellulose ether with a maximum water content of 75% is mixed with 0.1 to 10% strength aqueous hydrogen peroxide solution. The resulting mixture is then oxidatively degraded and dried at 100 to 250°C until the  $H_2O_2$  is consumed.

- DE-A-20 16 203 describes a process for the degradation of cellulose ethers in  
15 which a very substantially dry powder with a maximum water content of 5% is mixed with a hydrogen peroxide solution and degraded at 50 to 150°C.

In GB-B-953 944, the viscosity of water-soluble, nonionic cellulose ethers is reduced in the dry or moistened state by reaction with  $H_2O_2$  at elevated temperatures.

20

The oxidative degradation of cellulose ethers usually leads to the formation of numerous by-products.

If the degradation takes place on the moist or finished product without a subsequent purification step in order to optimize the yield, the by-products which

- 25 have formed are no longer removed from the depolymerized product. Very low-viscosity cellulose ethers prepared by oxidative degradation are normally colored because of the drastic reaction conditions.

Simple hydrolytic degradation processes with inorganic or organic acids are described, for example, in US-A-1 679 943, US-A-1 943 461, EP-B-0 497 985 and

- 30 EP-A-0 210 917.

In US-A-1 943 461, the preground cellulose ethers are degraded with dilute acids or mixtures thereof (concentration 0.5 to 5%, a multiple of the weight of the cellulose ether to be degraded) in a closed pressure vessel under a pressure of

0.7 to 5.2 bar and at temperatures of from 115 to 160°C for 20 to 60 minutes. US-A-1 679 943 describes the degradation of cellulose ethers with various acid mixtures without either a pressure vessel or an elevated temperature being required. However, especially at room temperature, this results in unacceptably long reaction times, which may be in the region of several days.

In EP-B-0 497 985, pulps with a low copper number, i.e. high  $\alpha$ -cellulose content, are washed, dried, ground and mixed with a 0.5% by weight aqueous HCl solution at a temperature of about 70°C. The water content of the cellulose ether plays an important part in this process. On the one hand, it must not fall below 1% during drying because excessive drying leads to hornification and yellowing of the products but, on the other hand, it must not be more than 5% during the degradation because considerable amounts of water favor gel formation with low molecular weight cellulose ethers. The resulting cellulose ethers have very low viscosities (< 20 mPas, 2.0% solution at 20°C). A similar process is described in EP-A-0 210 917. In this case, a cellulose ether powder containing 3 to 8% water is degraded with 0.1 to 1% by weight of an aqueous HCl solution at 40 to 85°C.

Degradation in particular to very low-viscosity products of high purity cannot be achieved by using HCl as gas. Processes of this type are described, for example, in US-A-3 391 135 and US-A-4 061 859.

US-A-3 391 135 discloses a process for preparing cellulose ethers with solution viscosities of less than 10 mPas (2.0% solution at 20°C) from high-viscosity cellulose ether powders with water contents of less than 5% at 30 to 80°C. Excess HCl gas is removed and the cellulose ether is then neutralized by admixing a weak base.

According to US-A-4 061 859, cellulose ethers are degraded as dry powders with a water content of from 0.01 to 5% by weight using hydrogen halide at 15 to 80°C, and then neutralized by mixing sodium bicarbonate or passing in ammonia gas. Bleaching of the material obtained is achieved with sulfur dioxide gas, with which the degraded material is brought into contact after the depolymerization stage. It is possible with this process to degrade cellulose ethers to very low-viscosity



products whose initial viscosity was several hundred thousand mPas. The bleaching stage following the depolymerization makes it possible to brighten the products.

- 5 Hydrolytic degradation is mild and neutral in relation to functional groups and can be employed for preparing very low-viscosity products. However, if the cellulose ether to be degraded is present in relatively great dilution in aqueous medium, it is scarcely possible to avoid losses of yields through partial developing of the material. If, on the other hand, completely worked up, ground and dried cellulose
- 10 ethers are degraded with a little aqueous or gaseous HCl, neutralization by admixture with weak bases is necessary. This increases the salt content of the finished product and by-products of the reaction are not removed from the product. If the water content during the degradation is too high it is possible only with difficulty to avoid partial dissolving and adhesion of the material.
- 15 Homogeneous distribution of the small amounts of acid and a maximally uniform degree of polymerization are then likewise difficult to achieve. If the reaction is carried out under particularly mild conditions it is possible only to reduce but not suppress yellowing. Although subsequent bleaching of the products increases the whiteness of the material, it means an additional process step and does not lead
- 20 to removal of the by-products formed.

It was therefore an object of the present invention to provide a process for the depolymerization of cellulose ethers which does not have the prior art disadvantages mentioned.

- 25 In particular, possible ways were sought for preparing very low-viscosity cellulose ethers which, besides maximally uniform degrees of polymerization and small by-product constituents, have a very low salt content and a high whiteness and are intended to provide clear solutions with high transmittances so that they can advantageously be employed in particular in the sectors of drugs coating (tablets,
- 30 coated tablets, capsules), cosmetics, foodstuffs and suspension polymerization.

This object is achieved by a process for the depolymerization of hot water-coagulable cellulose ethers by hydrolytic degradation by means of acids, which is

characterized in that the degradation is carried out at a temperature above the cloud point of the cellulose ether as concentrated aqueous slurry.

It is possible in this connection to use as cellulose ethers all cellulose ethers

5 known to be hot water-coagulable.

Preference is given to alkylcelluloses such as, for example, methyl-, ethyl- and propylcellulose, and mixed ethers thereof, such as for example, hydroxyethylmethyl-, hydroxypropylmethyl-, ethylhydroxyethyl- and

10 ethylmethylcellulose.

The preparation and working up of the cellulose ethers employed for the degradation is not restricted in any way at all. They can be prepared and worked up by all processes known to the skilled worker (Ullmann's Enzyklopädie der

15 Technischen Chemie; Volume 9, "Celluloseether", Verlag Chemie, Weinheim, 4th edition 1975, pp. 192 ff).

The degree of polymerization and the viscosity of the cellulose ethers to be employed is likewise not restricted in any way at all. However, the cellulose ether

20 employed for the degradation ought preferably to have a degree of polymerization not too far removed from the degree of polymerization which is intended to be achieved by the depolymerization.

In a particularly preferred embodiment, the process of the invention is used to

25 prepare very low-viscosity cellulose ethers which have Höppler viscosities measured as 2.0% solution (absolutely dry) in water at 20°C of  $\leq 50$  mPas.

Acids suitable for the hydrolytic degradation are mineral acids, but also strong organic acids, and mixtures thereof. However, mineral acids are preferred.

The mineral acids particularly preferably employed are hydrochloric acid, sulfuric acid, nitric acid and phosphoric acid. However, it is also possible to use mixtures thereof.

30

Strong organic acids employed are preferably trifluoroacetic acid, acetic acid, formic acid, oxalic acid, phthalic acid, maleic acid and benzoic acid. However, it is also possible to use mixtures thereof.

- 5 The acid-catalyzed hydrolytic degradation is carried out according to the invention above the cloud point of the cellulose ether. A temperature range from 70 to 105°C is preferred.

10 The process of the invention is additionally characterized in that degradation is carried out as concentrated slurry. The ratio of water to cellulose ether preferably does not exceed 10:1, particularly preferably does not exceed 7:1 and in particular does not exceed 5:1, by weight. The use of minimal amounts of water as suspending agent leads to very small losses of yield, which are generally caused by the dissolving of low-viscosity constituents.

15

In a further preferred embodiment, in addition oxidizing agents are added to the concentrated aqueous slurry before, during and/or after the depolymerization in acidic or neutral medium.

- 20 The oxidizing agents preferably employed are hydrogen peroxide and salts thereof, other peroxo compounds such as for example, sodium peroxosulfate, perborates (also in combination with activators such as TAED), sodium chlorite, halogens, halogen oxides and other compounds employed for bleaching. Hydrogen peroxide ( $H_2O_2$ ) is particularly preferred.

25

The oxidizing agents are generally employed in this connection in amounts of from 0.01 to 20% by weight, preferably 0.01 to 10% by weight and particularly preferably 0.01 to 5% by weight, based on the cellulose ether.

- 30 It has been found, surprisingly, that the addition of oxidizing agents even in small amounts of distinctly less than one percent, preferably during the hydrolytic degradation, in addition to reducing the viscosity leads to by-products of the reaction which are normally at least partly adsorbed onto the cellulose ether and

- cause a coloration thereof being converted by oxidation into a form with better solubility in water. This leads to an improved removal of the by-products from the depolymerized cellulose ether. Consequently, the use of oxidizing agents such as, for example,  $H_2O_2$ , leads to an improvement in the whiteness of the products with
- 5 a simultaneous increase in the degree of uniformity. Moreover, the addition of oxidizing agents ensures an additional reduction in the final viscosity under conditions which are otherwise identical. It is thus possible to ensure a defined target viscosity to shorten the reaction time and/or reduce the amount of acid compared with carrying out the process without the addition of oxidizing agents.
- 10 Addition of the oxidizing agent is in principle also conceivable before or after the hydrolytic degradation by means of acids, but addition during the depolymerization is preferred.
- 15 The degradation and additional brightening through oxidation and/or removal of by-products can be carried out either in one step or else in succession, specifically both in the acidic medium and after (partial) neutralization has taken place.
- A further possibility is to carry out the degradation both on the ready-formulated
- 20 product and on moist crude products with the usual moisture content. Since a subsequent drying and grinding is necessary for formulating the product, it is preferred for moist crude products as result in production processes to be used for the degradation.
- 25 The degradation may, for example, be carried out in place of the last washing step when the salt content has been partly reduced, because excess salt from the reaction to give the cellulose ether is likewise removed by the aqueous slurry. The resulting products have an extremely low salt content.
- 30 The aqueous solutions of the degraded cellulose ethers usually have slightly acidic pH values due to the generation of acidic groups on the basic cellulose ether framework. The pH of these solutions can be adjusted to a substantially neutral pH of 5.5 to 8.0 by using, after the depolymerization, not water but an

aqueous solution of at least one basic salt (such as, for example, sodium carbonate, sodium bicarbonate, sodium sulfate, sodium bisulfate) to wash the degraded cellulose ether, at a temperature above the cloud point of the degraded cellulose ether, to wash out the by-products of the reaction. An additional mixing  
5 step as described in other processes for adjusting a target pH is unnecessary. The base is uniformly distributed and the cellulose ether can in the normal process be dried and ground in one or more steps.

The yields of the described process are generally between about 80% and 96%,  
10 depending on the required final viscosity and the level of the cloud point of the cellulose ether to be degraded. Since in the aqueous working up of cellulose ethers a washing loss between 3 and 8% usually occur, depending on the viscosity, and the degradation can be carried out in place of a washing step, the losses of yield are minimized. It is possible to increase the yield, in particular with  
15 products having a high cloud point, by increasing the temperature of degradation when carried out in a pressure apparatus.

The viscosity of the resulting products can essentially be adjusted as desired via the amount of acid employed, the reaction time and, where appropriate, the amount of additional oxidizing agent, and is very reproducible. Because of the  
20 uniform degradation associated with good mixing and distribution of the reactants, the products have virtually uniform degrees of polymerization.

It is possible to prepare by the process of the invention cellulose ethers with high purity and high whiteness. Particularly good results are achieved in the  
25 preparation of methylhydroxypropylcelluloses.

The present invention thus further relates to methylhydroxypropylcelluloses with a Höppler viscosity measured on a 2.0% solution (absolutely dry) in water at 20°C preferably of  $\leq 50$  mPas and particularly preferably  $\leq 5$  mPas.

30

The whiteness of the methylhydroxypropylcelluloses with a viscosity in the range from 5 to 50 mPas is preferably above 60% and of methylhydroxypropylcelluloses whose viscosity is  $\leq 5$  mPas is preferably above 50% (basis: DIN standard 5033).

Since the whiteness depends inter alia on the particle size distribution of the cellulose ether, the stated values relate to products whose proportion of particles with a size of  $< 125 \mu\text{m}$  does not exceed 50%, but is preferably less than 10%.

5

The salt content of the prepared cellulose ethers is preferably below 0.4% by weight, particularly preferably below 0.2% by weight and especially below 0.1% by weight.

- 10 Particularly preferred methylhydroxypropylcelluloses have a content of methoxy groups in the range from 28 to 32% by weight and a content of hydroxypropyl groups in the range from 5 to 9% by weight.

- 15 The described cellulose ethers are, because of their purity and high whiteness, especially suitable for coating pharmaceuticals and seeds and for use in cosmetics, foodstuffs or in suspension polymerization.

The invention is described in detail below by means of exemplary embodiments without, however, being restricted thereby.

20

The viscosities were measured in the examples, unless expressly noted otherwise, 2.0% strength (absolutely dry), in aqueous solution using a Höppler falling ball viscometer supplied by Haake.

- 25 The stated amounts of acid mean, unless indicated otherwise, percentages by weight, of concentrated HCl (37% strength), based on the amount of cellulose ether employed.

#### Examples 1 to 12

- 30 14 kg of water are heated to boiling in a 30 l glass vessel supplied by QVF stirred with a paddle stirrer. The appropriate amount of concentrated hydrochloric acid is then slowly added, and 5 kg (absolutely dry) of starting material are scattered in as water-moist product (dry content about 60%). After this, 50 g of  $\text{H}_2\text{O}_2$  (100%) is

introduced as aqueous solution of any concentration through a dropping funnel, which corresponds to employing an amount of 1% by weight based on the cellulose ether.

The mixture is stirred at 90 to 100°C for the time stated in Table 1 and is then

- 5 neutralized to pH 6.5 to 7.5 by slow addition of an equimolar amount of dilute sodium hydroxide solution (1 part of concentrated NaOH (50% strength) + 3 parts of water) over the course of 30 minutes.

The resulting product is filtered hot with suction through a glass frit of appropriate pore size and washed with a little boiling water in order to remove residues of

- 10 suspending agent, some of which have considerable color, from the product. The product is then dried and comminuted in a commercially available mill. The grinding parameters chosen for this are such that the resulting granules have the following particle size distribution:

- |                            |        |
|----------------------------|--------|
| > 500 $\mu\text{m}$        | < 5 %  |
| 15 500 – 125 $\mu\text{m}$ | > 85 % |
| < 125 $\mu\text{m}$        | < 10 % |

The characteristic analytical data summarized in Table 1 are determined for the granules.

Table 1: Acid-catalyzed degradation of hot water-coagulable cellulose ethers (MHPC) with and without additional oxidizing agent

| Ex. No. | Starting material <sup>1)</sup> | HCl [% by wt] <sup>2)</sup> | Time [h] | H <sub>2</sub> O <sub>2</sub> | Whiteness powder [%] <sup>3)</sup> | Viscosity [mPas] | Salt [%] <sup>4)</sup> | Transm. [%] <sup>5)</sup> |     |
|---------|---------------------------------|-----------------------------|----------|-------------------------------|------------------------------------|------------------|------------------------|---------------------------|-----|
|         |                                 |                             |          |                               |                                    | 2.0 %            |                        | 578                       | 415 |
| 1       | A                               | 8                           | 0.5      | -                             | 57                                 | 13.3             | 0.04                   | 95                        | 87  |
| 2       | A                               | 8                           | 0.5      | +                             | 61                                 | 9.4              | 0.06                   | 96                        | 92  |
| 3       | A                               | 16                          | 1        | -                             | 49                                 | 3.4              | 0.04                   | 96                        | 87  |
| 4       | A                               | 16                          | 1        | +                             | 55                                 | 2.9              | 0.04                   | 96                        | 89  |
| 5       | B                               | 4                           | 0.5      | -                             | 51                                 | 17.4             | 0.04                   | 92                        | 82  |
| 6       | B                               | 4                           | 0.5      | +                             | 71                                 | 11.6             | 0.04                   | 92                        | 87  |
| 7       | B                               | 4                           | 0.5      | + <sup>6)</sup>               | 62                                 | 12.0             | 0.04                   | 95                        | 87  |
| 8       | B                               | 4                           | 0.5      | - <sup>7)</sup>               | 69                                 | 11.3             | 0.04                   | 95                        | 90  |
| 9       | C                               | 8                           | 0.5      | -                             | 60                                 | 23.1             | 0.16                   | 95                        | 87  |
| 10      | C                               | 8                           | 0.5      | +                             | 61                                 | 10.8             | 0.09                   | 95                        | 90  |
| 11      | C                               | 16                          | 0.5      | -                             | 59                                 | 9.6              | 0.09                   | 94                        | 87  |
| 12      | C                               | 16                          | 0.5      | +                             | 59                                 | 5.3              | 0.04                   | 95                        | 90  |

5 <sup>1)</sup> A Linters pulp 1, methylhydroxypropylcellulose, OCH<sub>3</sub> = 30.0%,  
OC<sub>3</sub>H<sub>6</sub> = 7.2%; water-moist crude product, dry content about 61%,  
initial viscosity before degradation (1.9% absolutely dry): 340 mPas

B Linters pulp 2, methylhydroxypropylcellulose, OCH<sub>3</sub> = 29.1%,  
OC<sub>3</sub>H<sub>6</sub> = 6.5%; water-moist crude product, dry content about 56%,  
10 initial viscosity before degradation (1.9%, absolutely dry): 50 mPas

C Linters pulp 3, methylhydroxypropylcellulose, OCH<sub>3</sub> = 29.8%,  
OC<sub>3</sub>H<sub>6</sub> = 6.9%; water-moist crude product, dry content about 62%,  
initial viscosity before degradation (1.9%, absolutely dry): 35 000  
mPas

15 <sup>2)</sup> percent by weight of concentrated hydrochloric acid (37% strength) based  
on the cellulose ether (absolutely dry)



- 3) basis: DIN standard 5033; measured with LF 90 colorimeter (manufactured by Dr. Bruno Lange) against white standard (enamel white standard; reflectance setting = 71.5%) by measuring the reflectance in % at a defined wavelength; UME 3 universal measuring unit, LF 90 color sensor, measurement geometry 0°/45°, normal light type C, glass cuvette, blue filter BG12/5 (447 nm), light protection cap d = 50 mm
- 4) NaCl content due to neutralization of hydrochloric acid with sodium hydroxide solution
- 5) Transmission measured in 1.0% strength aqueous solution (absolutely dry) at 578 nm and 415 nm against water as standard
- 6) with addition of 10 g of H<sub>2</sub>O<sub>2</sub>
- 7) with addition of 50 g of NaClO<sub>2</sub>

### Examples 13 and 14

15

The process is as described in Example 1 to 12 with the exception that 25 kg of water is initially present, instead of 14 kg, and 3.75 kg (absolutely dry) of moist crude product are used for the degradation.



**ART 34 AMDT**

## Patent claims:

1. A process for the depolymerization of hot water-coagulable cellulose ethers by hydrolytic degradation by means of acids, characterized in that the degradation  
5 is carried out at a temperature above the cloud point of the cellulose ether as concentrated aqueous slurry, and in that in addition oxidizing agents are added to the concentrated aqueous slurry, before, during and/or after the depolymerization in acidic or neutral medium.
- 10 2. The process as claimed in claim 1, characterized in that methyl-, ethyl-, propyl-, hydroxyethylmethyl-, hydroxypropylmethyl-, ethylhydroxyethyl- or ethylmethylcellulose is employed as cellulose ether.
3. The process as claimed in claim 1 or 2, characterized in that the degraded  
15 cellulose ether has a Höppler viscosity, measured as 2.0% solution (absolutely dry) in water at 20°C, of  $\leq 50$  mPas.
4. The process as claimed in at least one of the preceding claims, characterized in that mineral acids and/or organic acids are employed as acids.  
20
5. The process as claimed in claim 4, characterized in that hydrochloric, sulfuric, nitric and/or phosphoric acids are employed as mineral acids.
6. The process as claimed in at least one of the preceding claims,  
25 characterized in that the ratio of water to cellulose ether does not exceed 10:1 by weight.
7. The process as claimed in at least one of the preceding claims, characterized in that peroxo compounds, perborates, sodium chlorite, halogens  
30 and/or halogen oxides are employed as oxidizing agents.
8. The process as claimed in claim 7, characterized in that hydrogen peroxide is employed as oxidizing agent.

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9. The process as claimed in at least one of the preceding claims, characterized in that the oxidizing agent is employed in an amount of from 0.01 to 20% by weight based on the cellulose ether.
- 5 10. The process as claimed in at least one of the preceding claims, characterized in that, after the depolymerization, the degraded cellulose ether is washed with at least one aqueous solution of a basic salt at a temperature above the cloud point of the degraded cellulose ether in order to adjust the aqueous solution of the degraded cellulose ether to a pH in the range from 5.5 to 8.0.
- 10 11. The process as claimed in claim 10, characterized in that sodium carbonate, sodium bicarbonate, sodium sulfate and/or sodium bisulfate is employed as salt.
- 15 12. A methylhydroxypropylcellulose with a Höppler viscosity, measured as 2.0% solution (absolutely dry) in water at 20°C of  $\leq 50$  mPas, obtainable by a process as claimed in at least one of the preceding claims.
- 20 13. A methylhydroxypropylcellulose with a Höppler viscosity, measured as 2.0% solution (absolutely dry) in water at 20°C, of  $\leq 50$  mPas, characterized in that it has a whiteness, determined by measuring the reflectance in % at 447 nm against a white standard (enamel white standard; reflectance setting = 71.5%), which is above 50%, with a particle size distribution in which the proportion of particles with a size of  $< 125 \mu\text{m}$  does not exceed 50%.
- 25 14. A methylhydroxypropylcellulose as claimed in claim 13, with a Höppler viscosity of from 5 to 50 mPas, characterized in that the whiteness, determined by measuring the reflectance in % at 447 nm against a white standard (enamel white standard; reflectance setting = 71.5%), is above 60%.
- 30 15. A methylhydroxypropylcellulose as claimed in claim 13 or 14, characterized in that it has a salt content of less than 0.4% by weight.

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16. A methylhydroxypropylcellulose as claimed in at least one of Claims 13 to 15, characterized in that it has a content of methoxy groups in the range from 28 to 32% by weight and a content of hydroxypropyl groups in the range from 5 to 9% by weight.

5

17. The use of the methylhydroxypropylcelluloses as claimed in at least one of claims 13 to 16 for coating pharmaceuticals or seeds and for use in cosmetics, foodstuffs or in suspension polymerization.

AMENDED SHEET

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
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(75) Erfinder/Anmelder (nur für US): HAMMES, Alf [DE/DE]; Marie-Juchacz-Strasse 21, 55252 Mainz-Kastel (DE).
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- (71) Anmelder (für alle Bestimmungsstaaten mit Ausnahme von US): CLARIANT GMBH [DE/DE]; Brüningstrasse 50, 65929 Frankfurt am Main (DE).
- Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: LOW-VISCOUS CELLULOSE ETHERS THAT FLOCCULATE IN HOT WATER, METHOD FOR THE PRODUCTION THEREOF AND THEIR USE

(54) Bezeichnung: NIEDERVISKOSE, HEISSWASSER-FLOCKBARE CELLULOSEETHER, VERFAHREN ZU DEREN HERSTELLUNG DURCH DEPOLYMERISATION SOWIE DEREN VERWENDUNG

(57) Abstract: The invention relates to low-viscous cellulose ethers that flocculate in hot water and that have a high degree of purity and whiteness. The invention also relates to a method of producing the same by acidic-catalyzed hydrolytic depolymerization in the presence of an oxidation agent, as well as to the use thereof.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft niederviskose, heisswasser-flockbare Celluloseether von hoher Reinheit und hohem Weissgrad, Verfahren zu deren Herstellung durch Depolymerisation mittels sauer katalysiertem, hydrolytischem Abbau, gegebenenfalls in Gegenwart eines Oxidationsmittels sowie deren Verwendung.

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**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**Low-viscous cellulose ethers that flocculate in hot water, method for the production thereof and their use**

the specification of which

☐ is attached hereto

☒ was filed on September 01, 2000, as International Patent Application PCT/EP00/08538

and including all the amendments through the date hereof.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

**Prior Foreign Application(s) for which Priority is Claimed:**

Federal Republic of Germany, 199 41 893.4, of September 03, 1999

As a named inventor, I hereby appoint the following registered practitioner(s), respectively and individually, as my attorneys and/or agents, with full power of substitution and revocation, to prosecute this application, and transact all business in the U.S. Patent and Trademark Office:

**CUSTOMER NUMBER 25,255**



**25255**

PATENT TRADEMARK OFFICE

Please address all communications to **Clariant Corporation, Industrial Property Department, 4331 Chesapeake Drive, Charlotte, North Carolina 28216**, telephone number 704/395-6712, facsimile number 704/395-6727.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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